6. Measurement of Ozone

6.1 Introduction

Ozone is a highly reactive, colorless gas. Any method used to measure ozone in an atmosphere must consider these properties. Ozone must be measured at the sampling location, as samples cannot be taken back to a laboratory for analysis.

Two measurement methods for ozone are approved for use in the U.S. by the U.S. EPA: one is based on the chemiluminescence that occurs when ozone and ethylene react, and the other on the attenuation of ultraviolet (UV) radiation by ozone. The method based on UV spectrometry is almost universally used in practice. Specifications and criteria for both methods exist in federal regulation. The UV photometry-based method is approved for use in California for state air quality standards. Both state and federal requirements are applied directly by the California Air Resources Board (CARB) and the air districts in the ozone monitoring network in California.

6.2 Existing Monitoring Methods

The U.S. EPA has developed design and performance criteria for methods used to measure tropospheric ozone. The federal reference method (FRM) is based on gas-phase chemiluminescence (40 CFR Part 50, Appendix D), and the federal equivalent methods (FEMs) are based on UV photometry (40 CFR Part 53, and McElroy et al., 1997), with the exception of one method based on gas-solid chemiluminescence (U.S. EPA, 1996).

The state ambient air quality standard for ozone (California Code of Regulations, Title 17, Section 70200) stipulates that ultraviolet photometry is the method to be used to measure ozone. The standard also allows an equivalent method to be used, as described in the first footnote to the “Table of Standards” in Section 70200:

"Any equivalent procedure which can be shown to the satisfaction of the Air Resources Board to give equivalent results at or near the level of the air quality standard may be used."

To implement the general requirement of a UV photometry-based measurement method, CARB and air district staff employ specific UV photometry-based methods and procedures as prescribed by the U.S. EPA. These UV methods must be operated in accordance with the manufacturers' instructions and instrument-specific CARB standard operating procedures, both of which are consistent with the requirements.

Below are general descriptions of the chemiluminescence and UV methods for ozone measurement.

6.2.1 Gas-Phase Chemiluminescence Methods

The most common chemiluminescence method for O_3 is direct gas phase reaction of O_3 with olefin to produce electronically excited products, which decay with the emission of light. When ozone reacts with ethylene gas, an olefin, electronically excited formaldehyde is produced. As this excited species returns to the ground state, it gives off light in a band centered at 430 nanometers (nm) in proportion to the amount of ozone present. This chemiluminescence can be measured using a photomultiplier tube, and the concentration of ozone is calculated (CARB, 1987, and U.S. EPA, 1996).

The U.S. EPA has identified specific monitoring instruments based on gas-phase chemiluminescence as FRMs for ozone measurement. Any other measurement method or instrument must be compared against the reference method, and must perform on a par with the reference method to be deemed equivalent. A detailed discussion of the measurement method principle and the calibration procedures for chemiluminescence-based instruments is given in the Code of Federal Regulations (CFR) 40 CFR, Part 50, Appendix D, and U.S. EPA, 1996.

Humidity causes a positive bias in chemiluminescence methods. This can be compensated for by using humidified air for instrument calibration.

Because the reference method uses a potentially flammable gas as a reactant, and because there is an equivalent method for directly measuring ozone, chemiluminescence-based monitors are seldom used for routine air monitoring. In areas of high humidity, the interference has been problematic and the debate continues as to the instrument's complete reliability for such an important purpose.

6.2.2 Ultraviolet Photometry Methods

Ozone exhibits a strong absorption band in the ultraviolet region at 254 nm. This feature is the basis of the photometric measurement method for ozone. Many commercially-available UV instruments meet U.S. EPA equivalency criteria as set forth in 40 CFR Part 53, § 53.32. A discussion of the principle of the UV spectrometric method for ozone is given in CARB, 1987, McElroy, et al., 1997, and U.S. EPA, 1996. Calibration techniques and other quality control and quality assurance methods and practices for the state method are described in the CARB Air Monitoring Quality Assurance Manual Volume II (Appendix A, 1995); see the on-line copy of the manual at:
http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.html

Other species present in the atmosphere such as aromatic hydrocarbons also absorb at or near 254 nm, and so represent potential interferences to the method. The commercially-available instruments compensate for this possible interference by comparing the absorbance of the sample with the absorbance of air in which the ozone has been catalytically reduced to molecular oxygen (O_2); consequently attenuation of the UV light due to non-ozone species is taken into account.

6.3 Recommendations

Staff recommends that the Board continue to endorse the UV method as the approved method in California for determining compliance with the state Ambient Air Quality Standard for ozone. By reference, therefore, staff recommend all federally approved UV methods be incorporated as California Approved Samplers for ozone. This will result in no change in air monitoring practices, but will align state monitoring requirements with federal requirements. Specifically, we recommend that a new part be added to the California Administrative Code 70100.1, to read:

"(c) Ozone Methods. For the purposes of determining compliance with the ozone ambient air quality standard, a designated federal method for ozone that uses ultraviolet light absorption as the measurement principle, as identified by the US EPA in Title 40, Part 53 of the Code of Federal Regulations, shall be California Approved Samplers.

The list of UV methods (U.S. EPA/ORD, 2002) is given at http://www.epa.gov/ttn/amtic/criteria.html"

Methods for Measuring Ozone

The following methods and instruments are *California Approved Samplers for ozone* for the purposes of determining compliance with the state ambient air quality standard:

Ultraviolet Method for the Determination of ozone in the Atmosphere, 40 CFR, Chapter 1, Part 50, Appendix D as published in FR 62, 38895, July 18, 1977. The specific instruments approved are:

a) Dasibi Models 1003-AH, 1003-PC, or 1003-RS Ozone Analyzers, U.S. EPA Automated Equivalent Method EQOA-0577-019, as published in FR 42, 28571, June 03, 1977.

b) Dasibi Models 1008-AH, 1008-PC, or 1008-RS Ozone Analyzers, U.S. EPA Automated Equivalent Method EQOA-0383-056, as published in FR 48, 10126, March 10, 1983.

c) DKK-TOA Corp. Model GUX-113E Ozone Analyzer, U.S. EPA Automated Equivalent Method EQOA-0200-134, as published in FR 65, 11308, March 02, 2000.

d) Environics Series 300 Ozone Analyzer, U.S. EPA Automated Equivalent Method EQOA-0990-078, as published in FR 55, 38386, September 18, 1990.

e) Environnment S.A. Model $O_3$41M UV Ozone Analyzer, U.S. EPA Automated Equivalent Method EQOA-0895-105, as published in FR 60, 39382, August 02, 1995.

f) Environnment S.A. Model $O_3$42M UV Ozone Analyzer, U.S. EPA Automated Equivalent Method EQOA-0206-148, as published in FR 67, 42557, June 24, 2002.

g) Environment S.A. SANOA Multigas Longpath Monitoring System, U.S. EPA Automated Equivalent Method EQOA-0400-137, as published in FR 65, 26603, May 08, 2000.

h) Horiba Instruments Models APOA-360 and APOA-360-CE Ozone Monitor, U.S. EPA Automated Equivalent Method EQOA-0196-112, as published in FR 61, 11404, March 20, 1996.

i) Monitor Labs/Lear Siegler Model 8810 Ozone Analyzer, U.S. EPA Automated Equivalent Method EQOA-0881-053, as published in FR 46, 52224, October 26, 1981.

j) Monitor Labs/Lear Siegler Models ML9810, ML9811, or ML9812, Monitors Labs Model ML9810B, or Wedding & Associates Model 1010 Ozone Analyzers, U.S. EPA Automated Equivalent Method EQOA-0193-091, as published in FR 58, 6964, February 03, 1993.

k) Opsis Model AR 500 and System 300 Open Path Ambient Air Monitoring Systems for Ozone, U.S. EPA Automated Equivalent Method EQOA-0495-103, as published in FR 60, 21518, May 02, 1995.

l) PCI Ozone Corporation Model LC-12 Ozone Analyzer, U.S. EPA Automated Equivalent Method EQOA-0382-055, as published in FR 47, 13572, March 31, 1982.

m) Philips PW9771 03 Analyzer, U.S. EPA Automated Equivalent Method EQOA-0777-023, as published in FR 42, 38931, August 01, 1977; FR 42, 57156, November 01, 1977.

n) Teledyne-Advanced Pollution Instrumentation, Inc. Model 400E Ozone Analyzer, Advanced Pollution Instrumentation, Inc. Model 400/400A Ozone Analyzer, U.S. EPA Automated Equivalent Method EQOA-0992-087, as published in FR 57, 44565, September 28; 1992, FR 63, 31992, June 11, 1998; FR 67, 57811, September 12, 2002.

o) Thermo Electron/Thermo Environmental Instruments Models 49, 49C, U.S. EPA Automated Equivalent Method EQOA-0880-047, as published in FR 45, 57168, August 27, 1980.

6.4 Estimated Costs and Impacts

Because the recommended change reflects the existing practice in air monitoring for ozone, approval of the recommendation will result in no costs or savings to any public agency, or to any private business.

6.5 References

California Air Resources Board. Effects of ozone on health, technical support document, pages 5-13.

Code of Federal Regulations. Title 40, Part 50, Appendix D, Measurement principles and calibration procedure for the measurement of ozone in the atmosphere.

Code of Federal Regulation. Title 40, Part 53, Revised requirements for designation of reference and equivalent methods for PM2.5 and ambient air quality surveillance for particulate matter. pages 1-28.

McElroy F, Dennis M, Monica N (1997). Determination of ozone by ultraviolet analysis. A new method for Volume II, Ambient air specific methods, quality assurance handbook for air pollution measurement systems.

U.S. EPA (1996). Air Quality Criteria for ozone and related photochemical oxidants, EPA/600/P-93/004q-cF, pages 3-90 to 3-102. http://cfpub.epa.gov/ncea/cfm/ozone.cfm

Title 17, Barclay California Code of Regulation, Section 70200.

U.S. EPA/ORD (2002). List of designated reference and equivalent methods. http://www.epa.gov/ttn/amtic/criteria.html

Appendix A (1995). Dasibi model 1003 AH ozone analyzer. Volume II: standard operating procedures for air monitoring, air monitoring quality assurance, California Air Resources Board. http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.htm